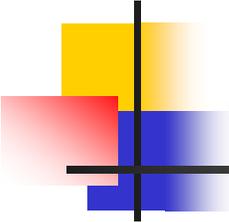


Application of PMCAMx+ to a July 2001 PM episode in the Eastern United States

Bonyoung Koo², Kathleen M. Fahey¹, Timothy M. Gaydos¹, Greg Yarwood², Ralph Morris² Spyros N. Pandis¹, and Allen Robinson^{1*} (speaker)

¹Carnegie Mellon University, Pittsburgh, PA, 15213.

²ENVIRON, Novato, CA, 94945

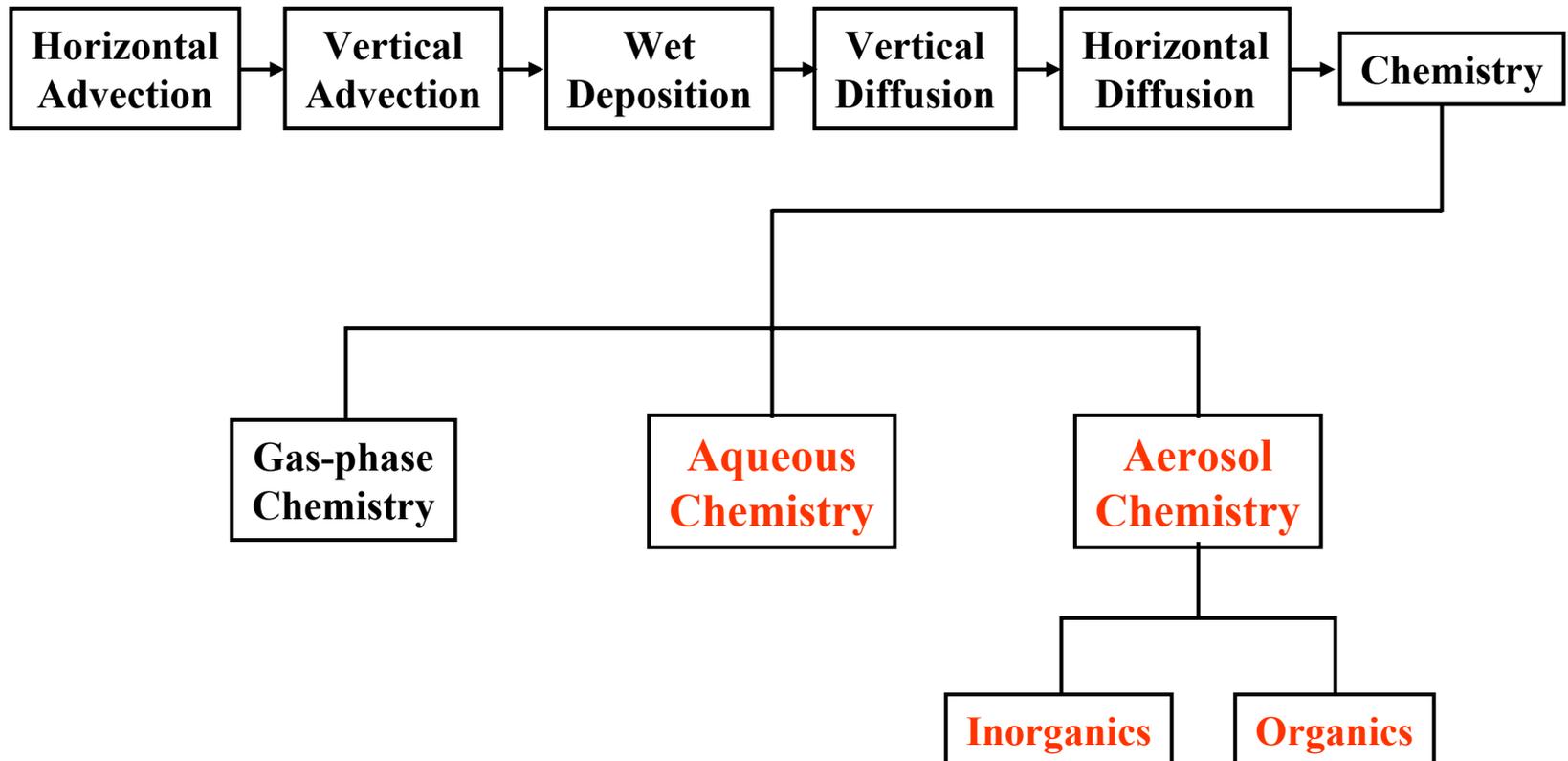


Overview

- Detailed aerosol modules developed for 3-D chemical transport model PMCAMx+
- Motivation: Improve efficiency while maintaining accuracy in three areas:
 - Inorganic aerosol growth
 - Aqueous-phase chemistry
 - Organic aerosol formation and growth
- Apply PMCAMx+ to PM episodes
 - October 1995 episode in SCAB, California
 - July 2001 episode in Eastern United States

PMCAMx+

PMCAMx+ = Comprehensive Air-quality Model with Extensions (CAMx)¹ with CMU Aerosol Modules
(<http://www.camx.com>)



Modeling Aerosol Growth

■ Bulk equilibrium (EQUI)¹

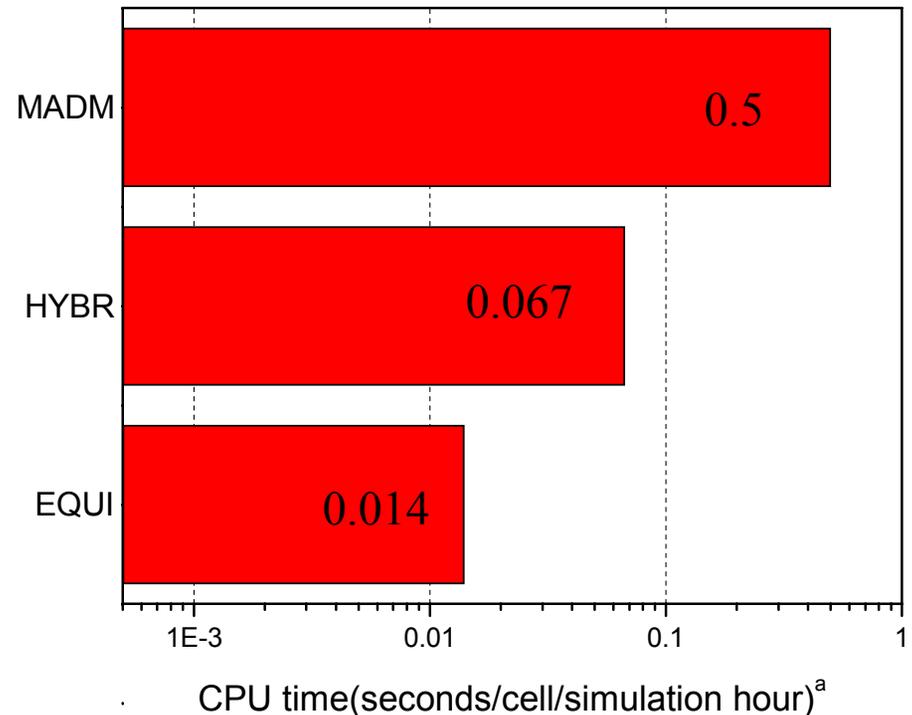
- Finds equilibrium between gas and total particulate phase
- Simplest and most efficient
- Overpredicts in smallest sections

■ Dynamic (MADM)²

- Solves mass transfer explicitly
- Most accurate but least efficient

■ Hybrid (HYBR)^{1,2}

- Uses bulk equilibrium for smallest particles and solves mass transfer for largest

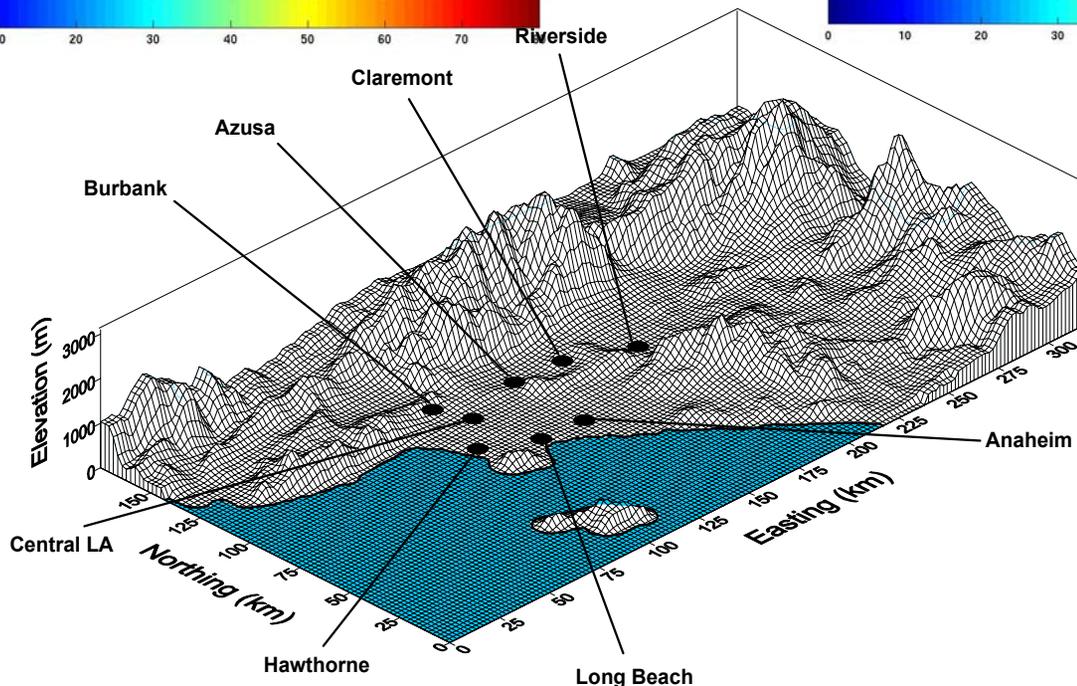
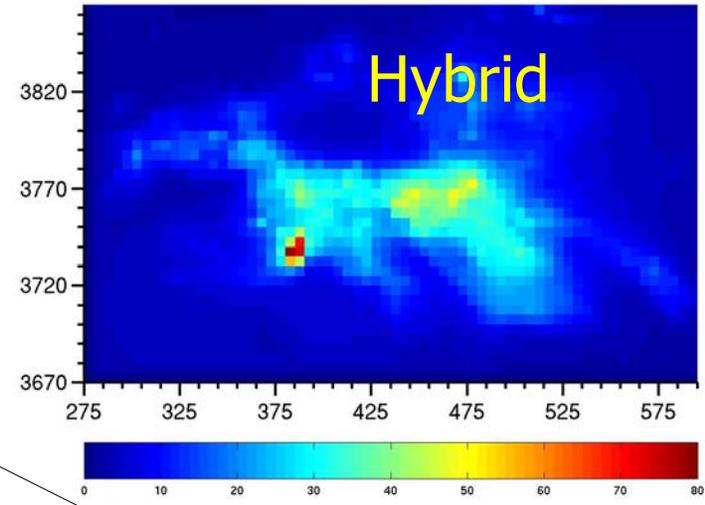
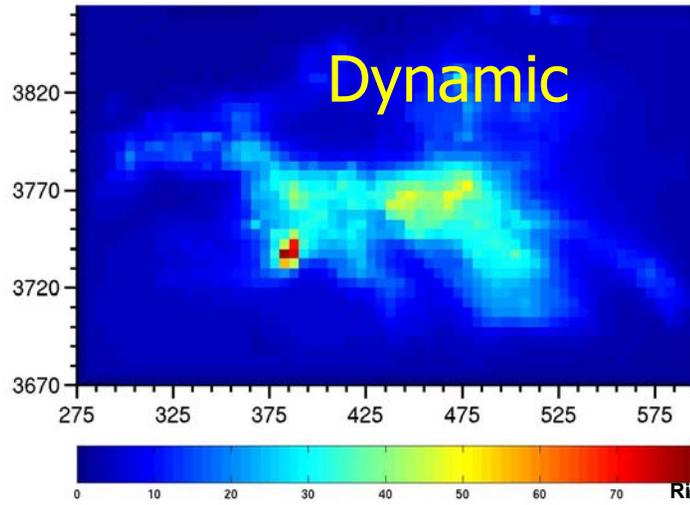


^aOn a 1.2 GHz AMD CPU with 1Gb RAM

¹Capaldo et al. (2000)

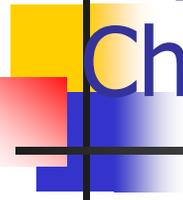
²Gaydos et al. (2003)

Hybrid Approach to Aerosol Dynamics in PMCAMx+ (SCAB)



The Hybrid approach is an order of magnitude faster.

Aqueous-Phase Atmospheric Chemistry Modeling



■ Bulk Models

- Homogeneous droplet population
- Can underpredict sulfate production
- Usually predicts lower sulfate production than size-resolved models

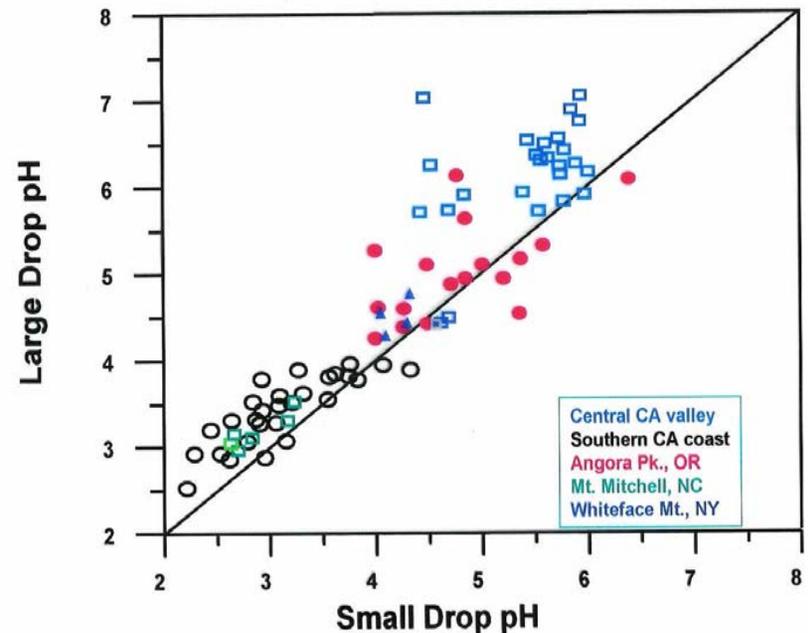
■ Size-Resolved Models

- Heterogeneous droplet population
- More computationally-intensive than a bulk model

■ Variable Size Resolution Model*

- Combines the accuracy of the size-resolved with the computational efficiency of the bulk

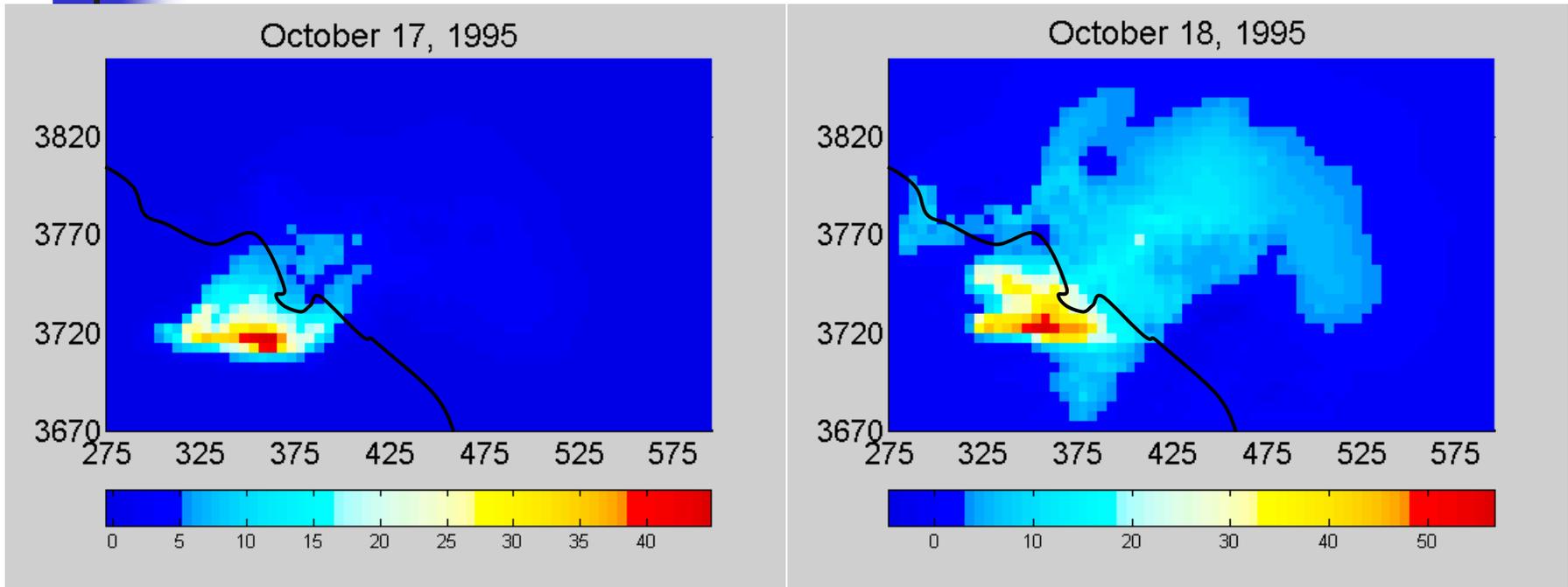
pH Differences Between Small and Large Cloud Drops
(Collett et al., 1994)



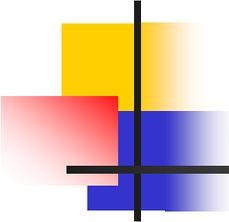
*Fahey et al. (2001)

Percent Increase in Sulfate

between Bulk and VSRM Aqueous-Phase Chemistry (SCAB)



- On the second day, much of the domain shows a sulfate underprediction of $\sim 15\text{-}30\%$ with a maximum of nearly 60% without added droplet size-resolution.
- VSRM only adds about 50% more computational time



SOA Model Description

- SOA partitioning is typically modeled as a solution of n condensable products P_1 to P_n



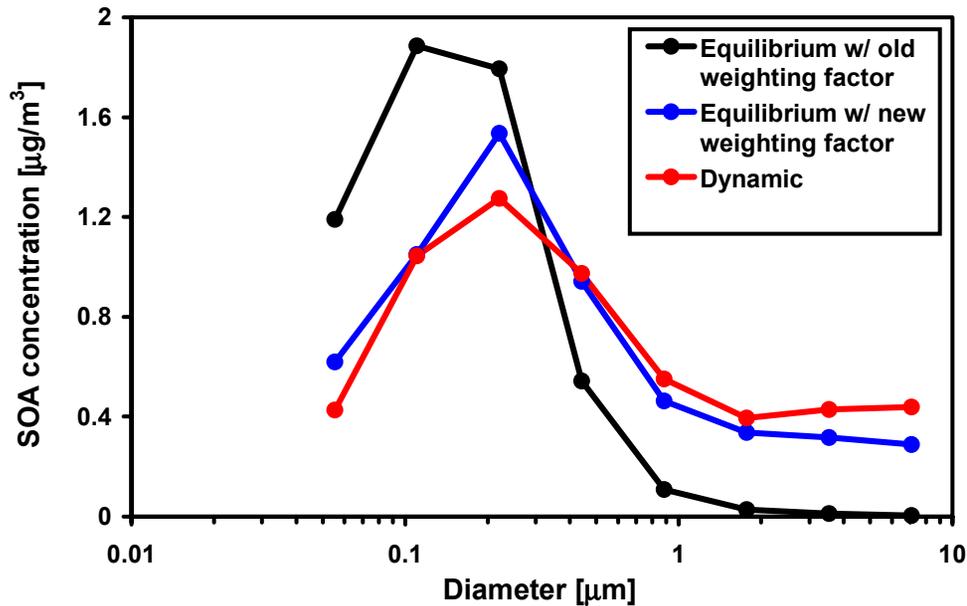
- Pseudo-ideal solution theory predicts SOA formation from condensable products

$$c_{gas,i}^{eq} = x_i c_i^*$$

- For each product a stoichiometric yield α_j and saturation concentration $c_j^*(T)$ are determined from empirical data
- Temperature dependence is included assuming saturation concentrations follow the Clausius-Clapeyron equation

$$\frac{c_i^*(T_2)}{c_i^*(T_1)} = \frac{T_1}{T_2} \exp \left[\frac{-\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right]$$

SOA module in PMCAMx+



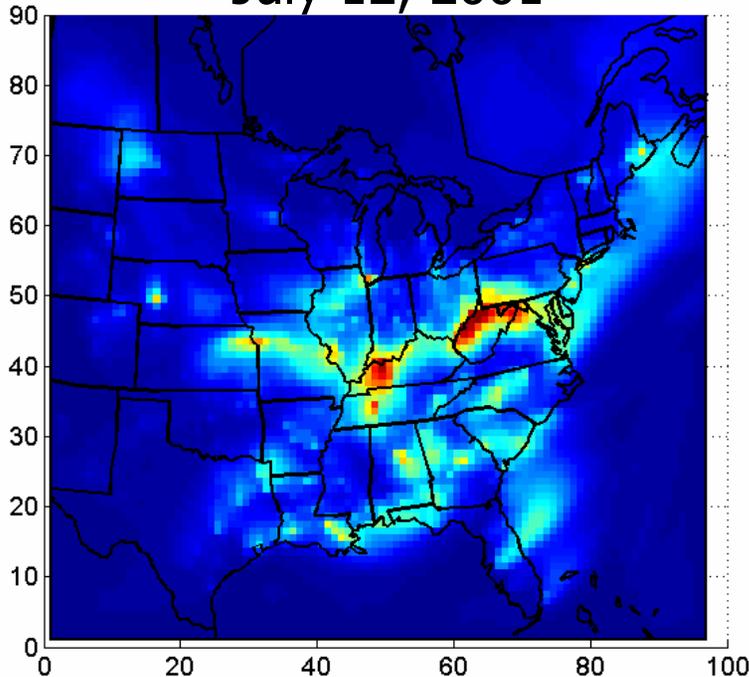
- Used pseudo-ideal solution theory to develop improved equilibrium weighting factor for secondary organics*
- Computational time comparable to original equilibrium method with results similar to dynamic scheme

*Koo et al. (2003)

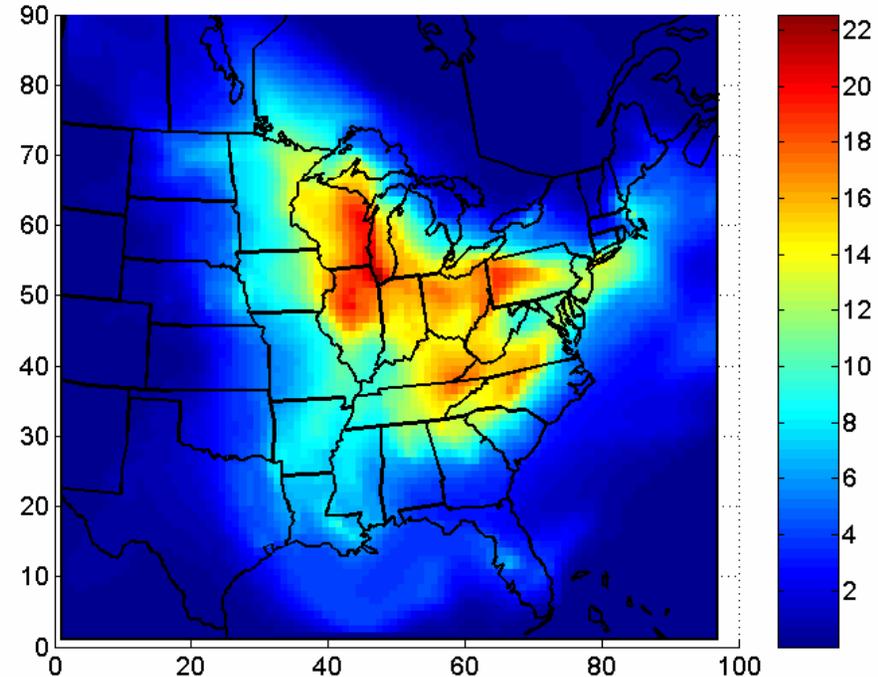
PMCAMx+ Modeling Domain

PM_{2.5} Sulfate

July 12, 2001



July 17, 2001



- 36x36 km grid, 14 levels up to 6 km
- 10 aerosol sections, 13 aerosol species
- 20 million differential equations
- 8 CPU hours on a PC per simulation day (EQUILibrium module)

Simulated Species

Gas species:
34 species

NO	Nitric oxide
NO2	Nitrogen dioxide
O3	Ozone
PAN	Peroxyacyl nitrates
NXOY	Nitrogen in NO3 and N2O5
OLE	Anthropogenic olefins
PAR	Paraffin
TOL	Toluene
XYL	Xylene
FORM	Formaldehyde
ALD2	Higher aldehyde
ETH	Ethene
CRES	Cresol
MGLY	Methylglyoxal
OPEN	Aromatic ring opening product
PNA	Peroxynitric acid
CO	Carbon monoxide
HONO	Nitrous acid
H2O2	Hydrogen peroxide
HNO3	Nitric acid
ISOP	Isoprene
MEOH	Methanol
ETOH	Ethanol
ISPD	Isoprene product
NTR	Organic nitrates
OLE2	Biogenic olefins
CG1	Condensable gas precursor to SOA1
CG2	Condensable gas precursor to SOA2
CG3	Condensable gas precursor to SOA3
CG4	Condensable gas precursor to SOA4
NH3	Ammonia
HCL	Hydrogen chloride
SO2	Sulfur dioxide
SULF	Gas phase sulfuric acid

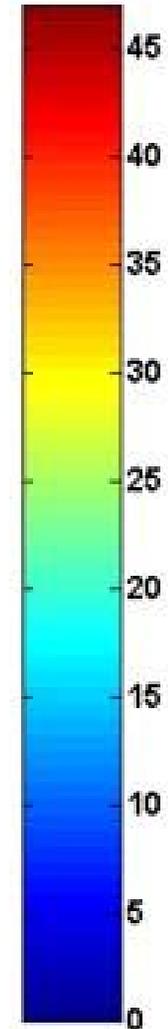
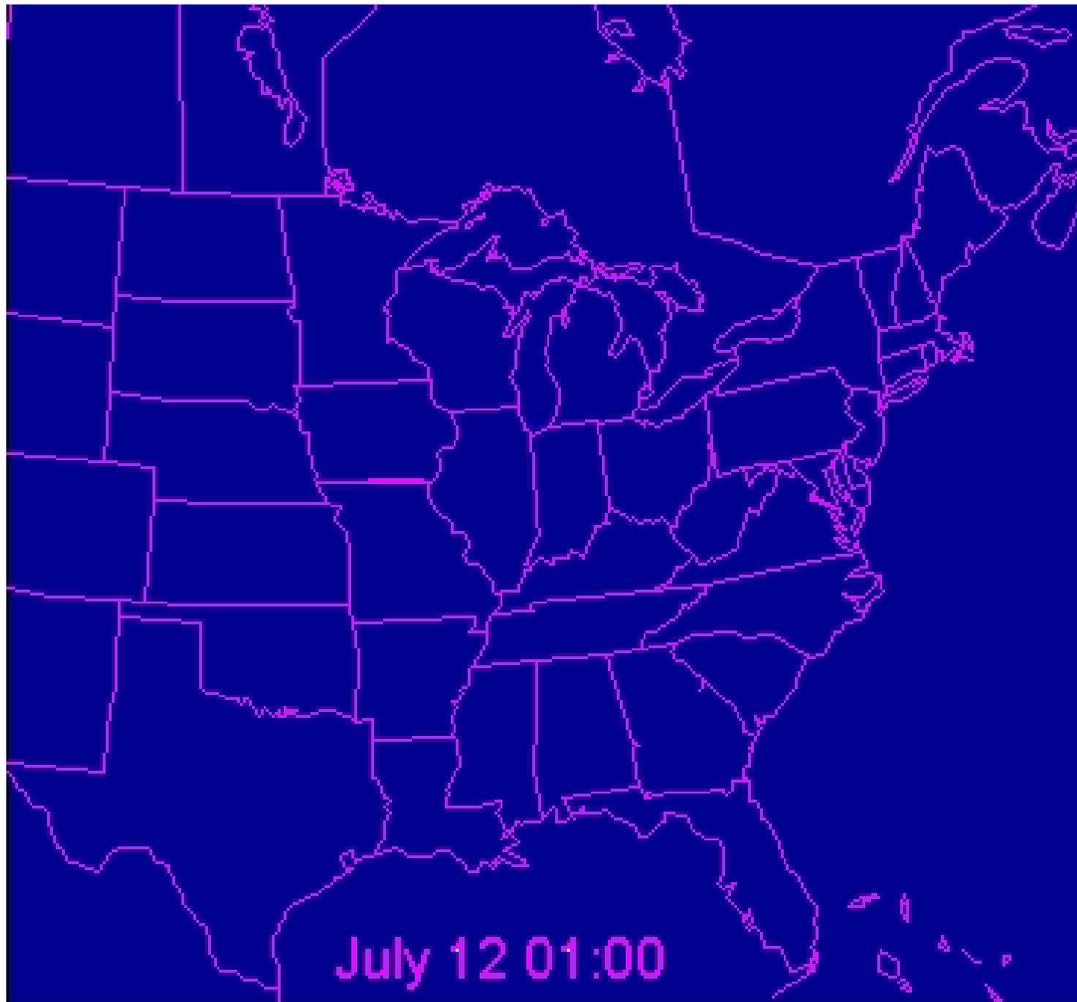
Aerosol species: 13 species

PH2O	Aerosol water
PSO4	Sulfate
PNO3	Nitrate
PCL	Chloride
NA	Sodium
PNH4	Ammonium
POC	Primary organic carbon
PEC	Primary elemental carbon
CRST	Crustal material
SOA1	Secondary organic aerosol 1
SOA2	Secondary organic aerosol 2
SOA3	Secondary organic aerosol 3
SOA4	Secondary organic aerosol 4

Aerosol size sections:

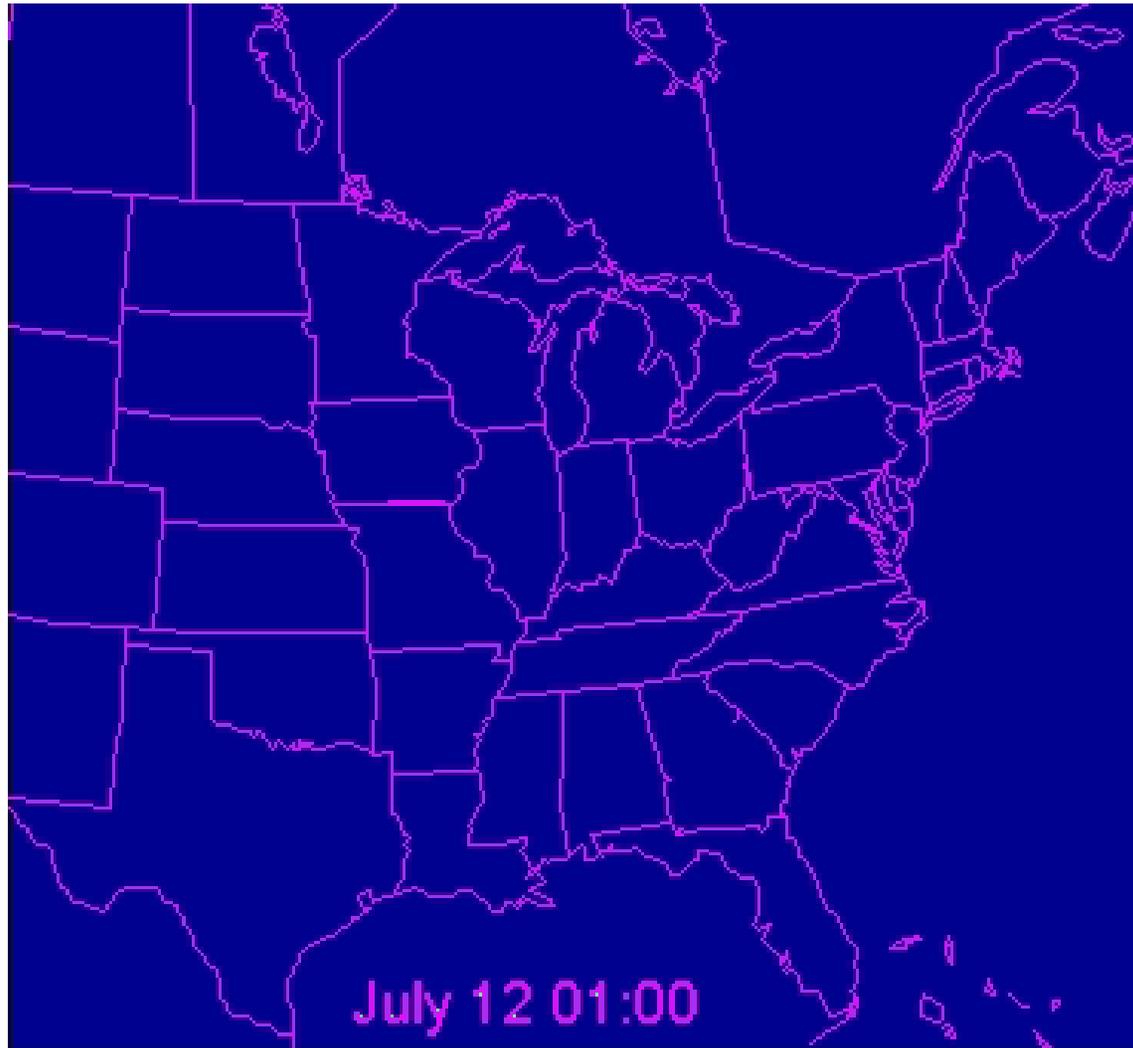
1	0.039 – 0.078
2	0.078 – 0.156
3	0.156 – 0.313
4	0.313 – 0.625
5	0.625 – 1.25
6	1.25 – 2.5
7	2.5 – 5
8	5 – 10
9	10 – 20
10	20 – 40

PM_{2.5} Sulfate Simulation (July 2001)

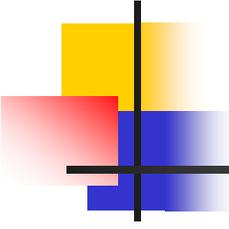


Click on map to start simulation.

PM_{2.5} Nitrate Simulation (July 2001)

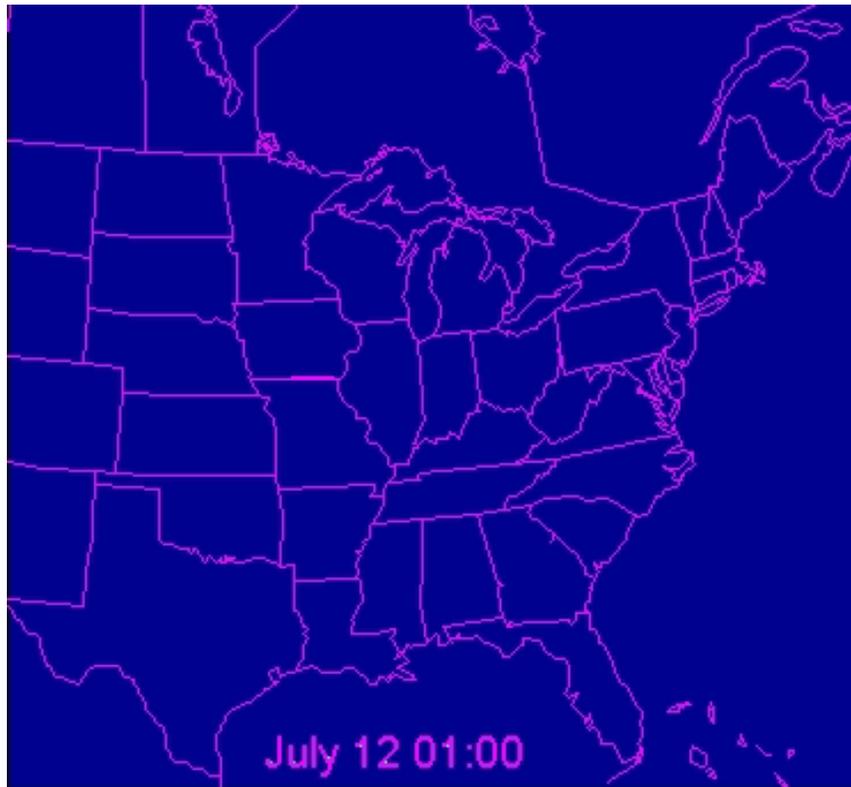


Click on map to start simulation.



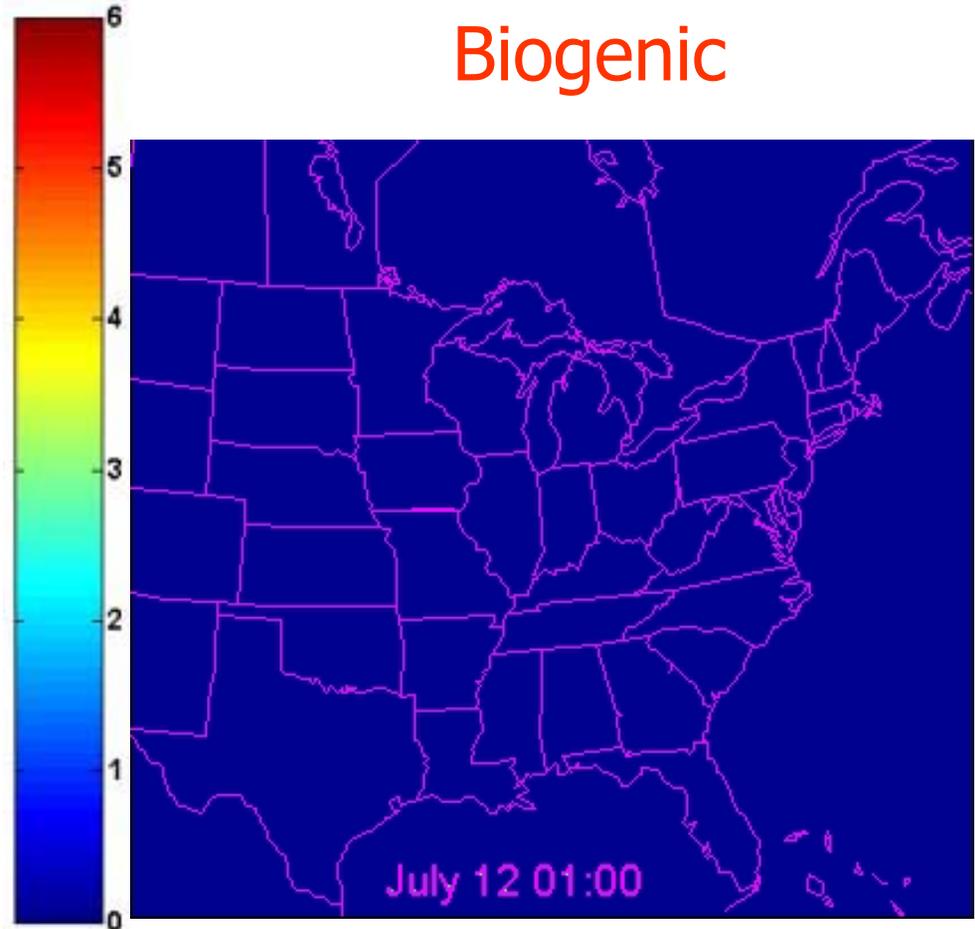
SOA Simulation (July 2001)

Anthropogenic



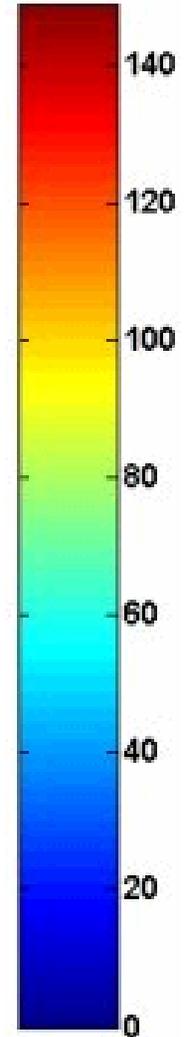
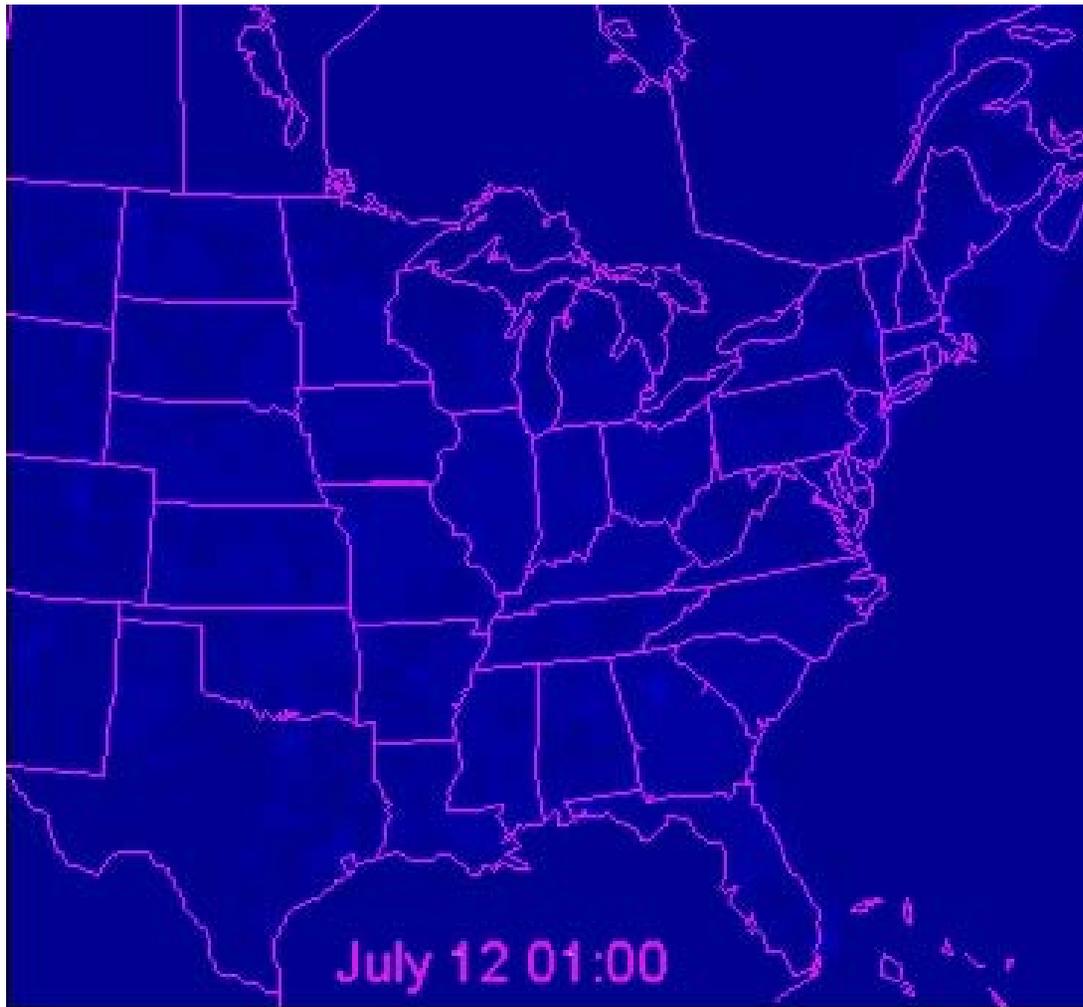
Click on map to start simulation.

Biogenic



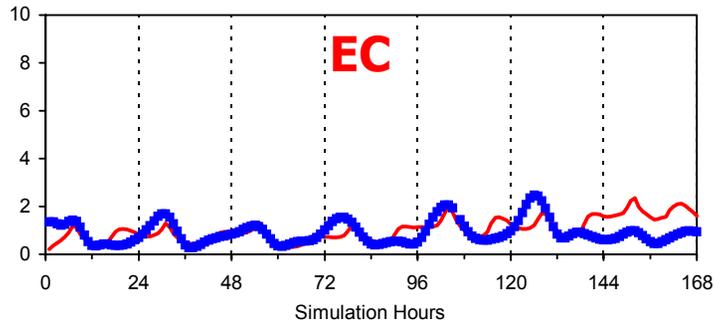
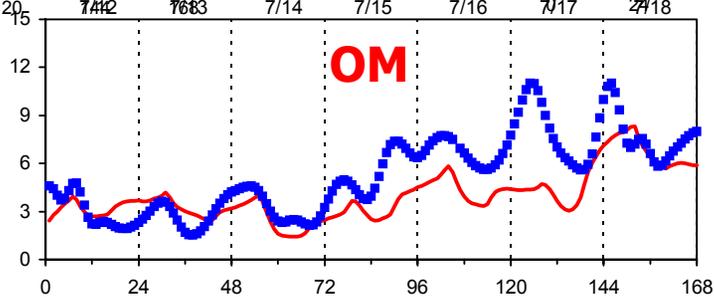
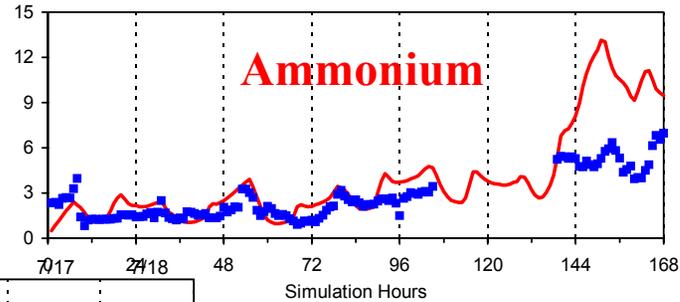
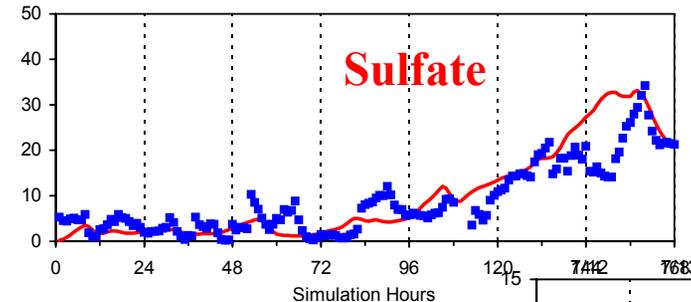
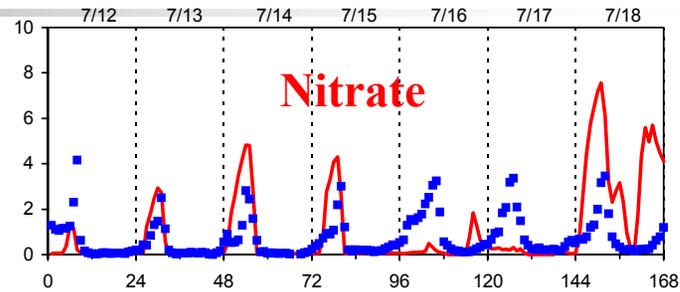
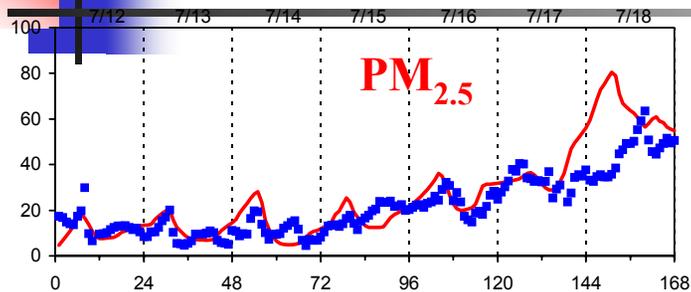
Click on map to start simulation.

PM_{2.5} Mass Simulation (July 2001)

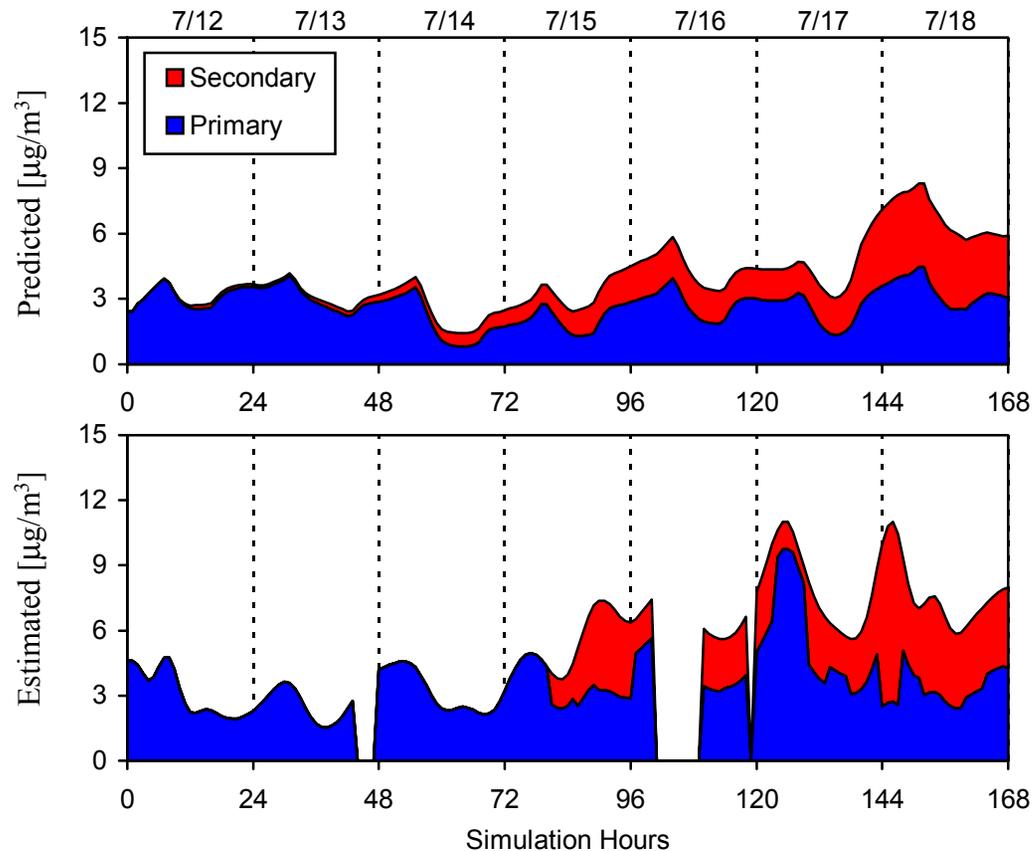


Click on map to start simulation.

PMCAMx+ Evaluation in Pittsburgh



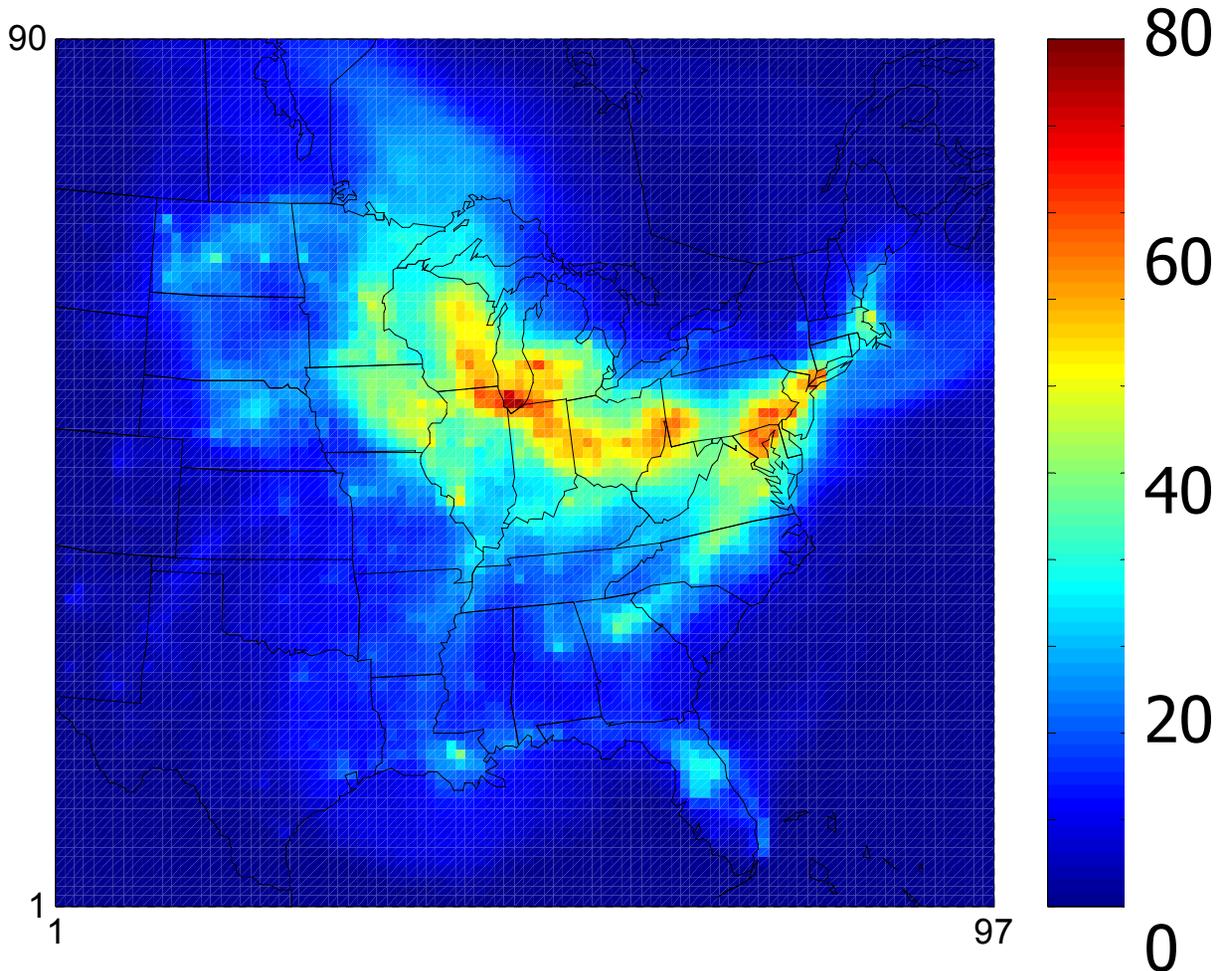
Predicted vs. Estimated in Pittsburgh (Primary and Secondary OA)



- EC Tracer Method (Cabada et al., 2003)

Predicted PM_{2.5} Concentrations

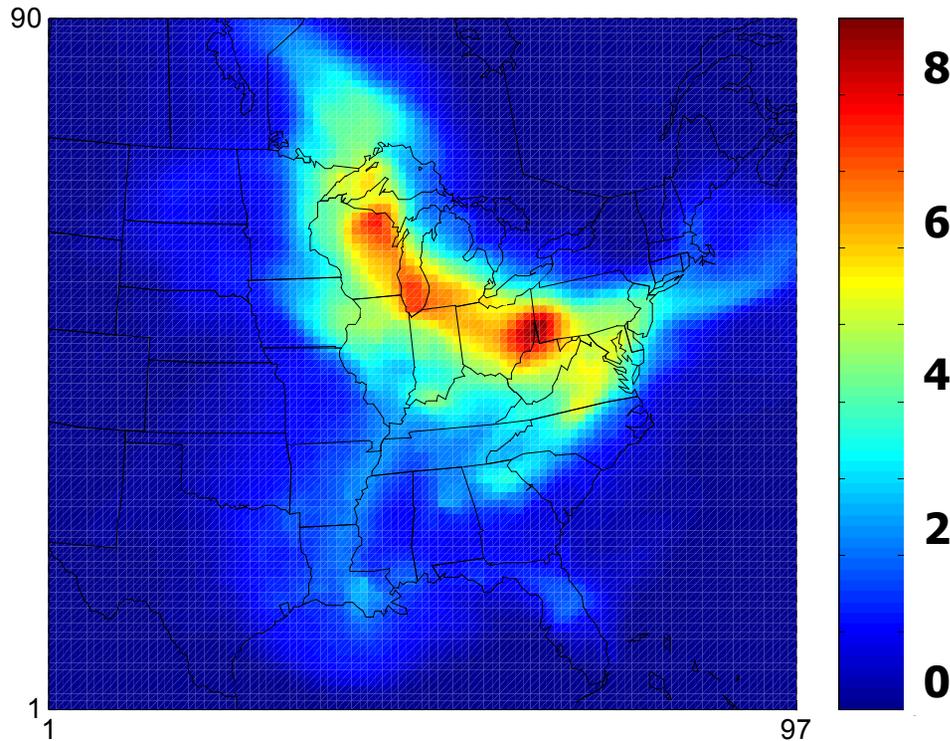
July 18, 2001



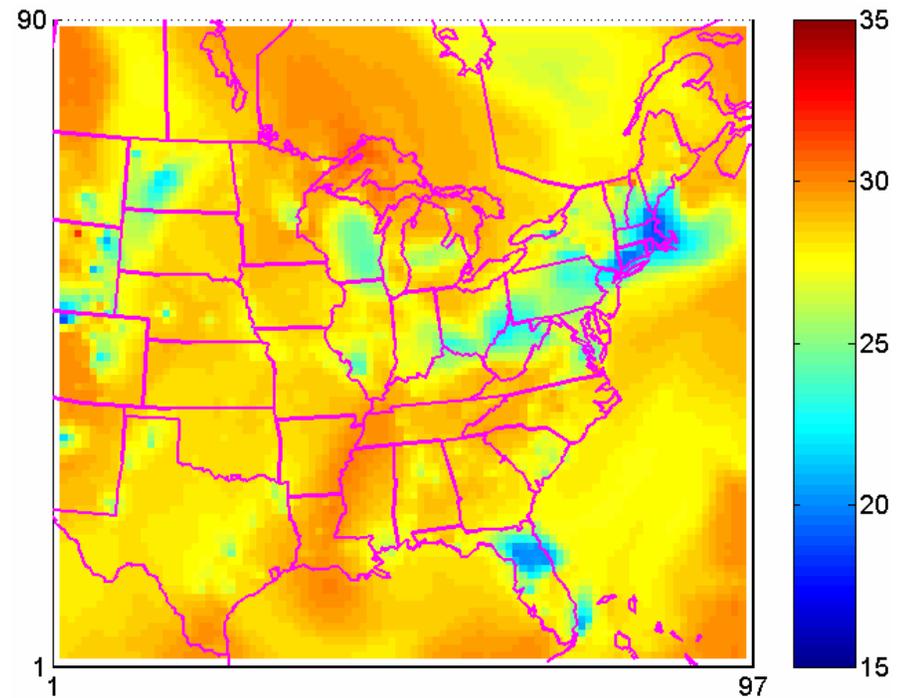
Sulfate Response (%) to 30% SO₂ Emission Reduction

July 18, 2001

Concentration Change ($\mu\text{g m}^{-3}$)



Percent Change

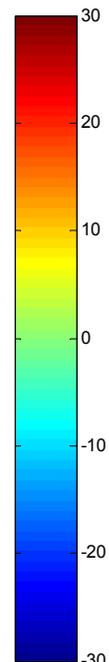
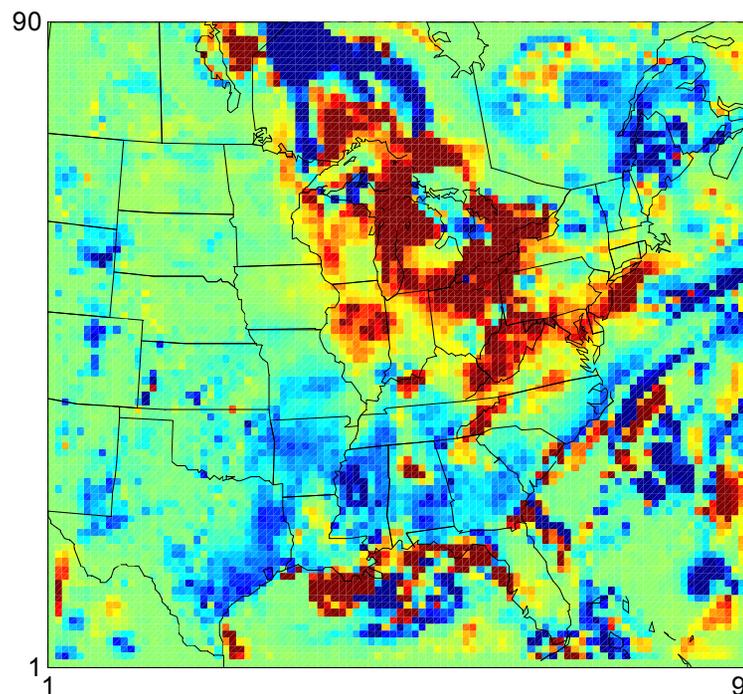
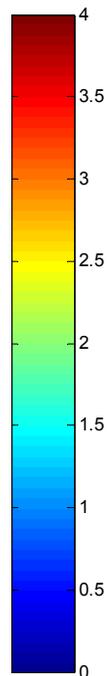
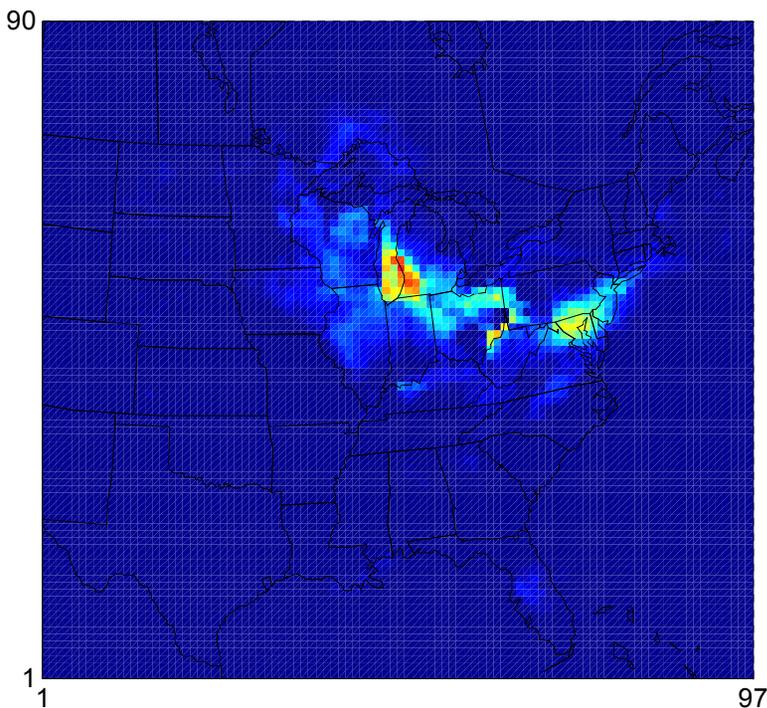


Nitrate Response (%) to 30% SO₂ Emission Reduction

July 18, 2001

Concentration Change ($\mu\text{g m}^{-3}$)

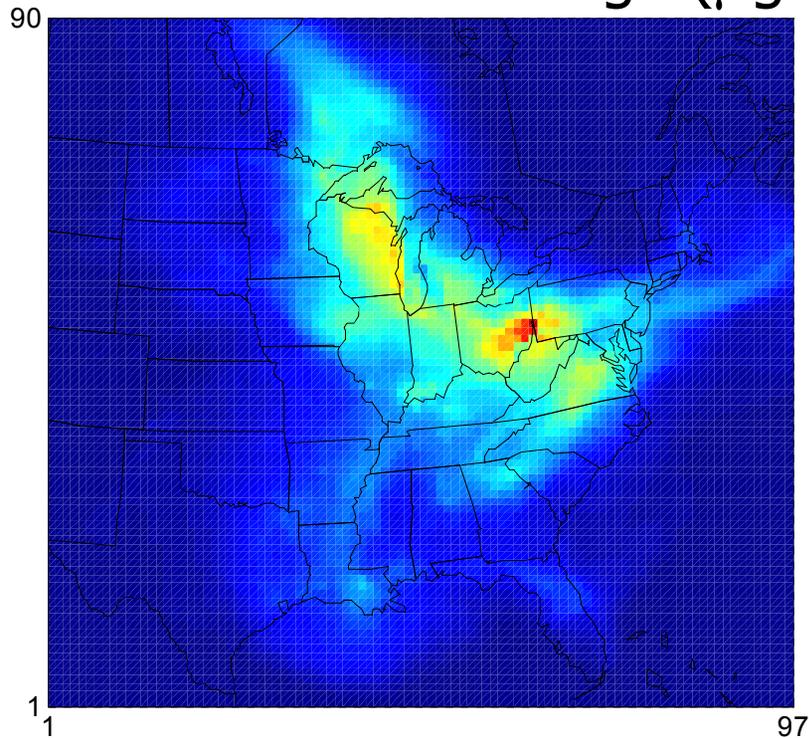
Percent Change



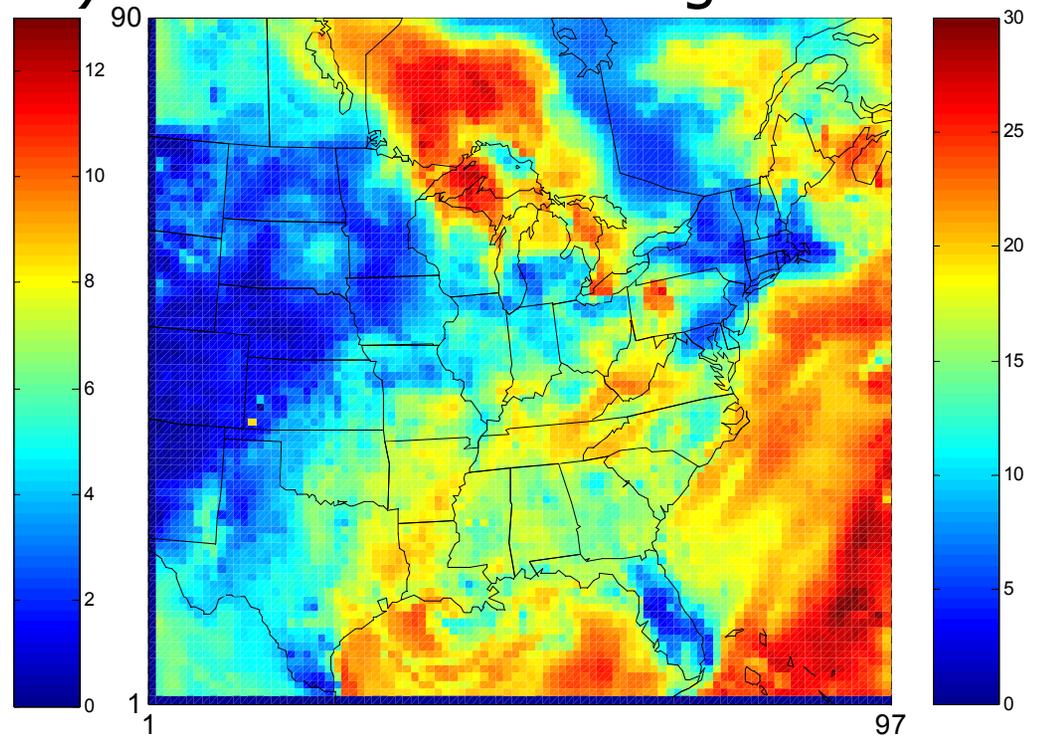
PM_{2.5} Response (%) to 30% SO₂ Emission Reduction

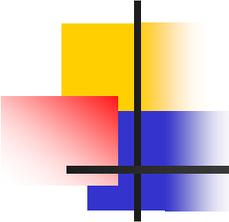
July 18, 2001

Concentration Change ($\mu\text{g m}^{-3}$)



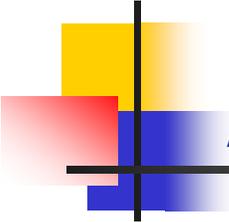
Percent Change





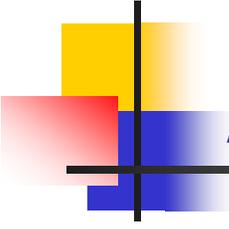
Conclusions

- CMU aerosol modules have been implemented into PMCAMx+, providing better efficiency and good accuracy
- Model predictions compare well to measurements in Eastern United States
 - Diurnal pattern of species replicated
 - PM_{2.5} sulfate, nitrate, ammonium, and total mass compare well to measurements
 - Presence and magnitude of secondary organic aerosol in good agreement with measurements
 - Both biogenic and anthropogenic SOA contribute to PM in Eastern US



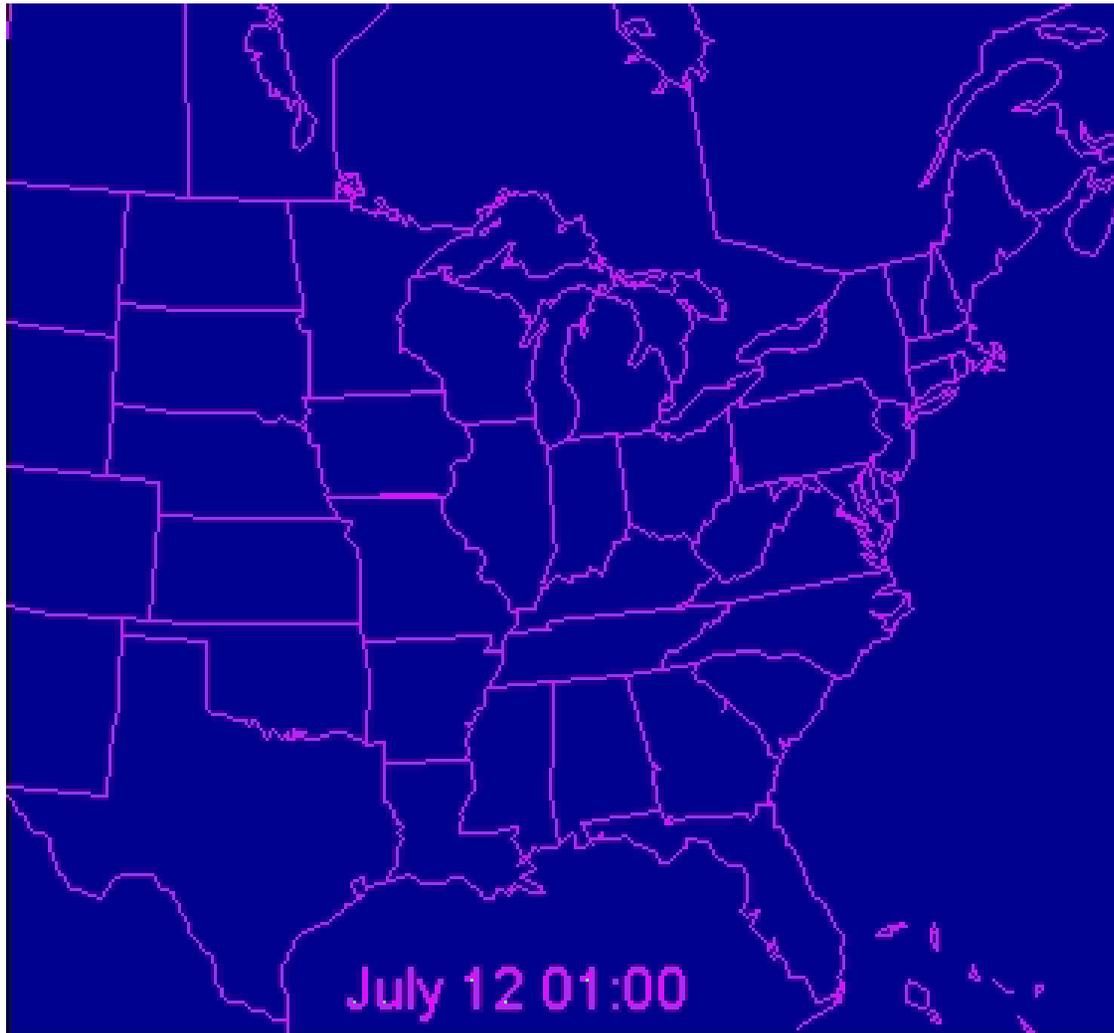
Acknowledgements

- **LADCO**
 - **Kirk Baker**
 - **Mark Janssen**
 - **Mike Koerber**
- **Funding**
 - **EPA**
 - **DOE/NETL**
 - **CRC**



Additional slides

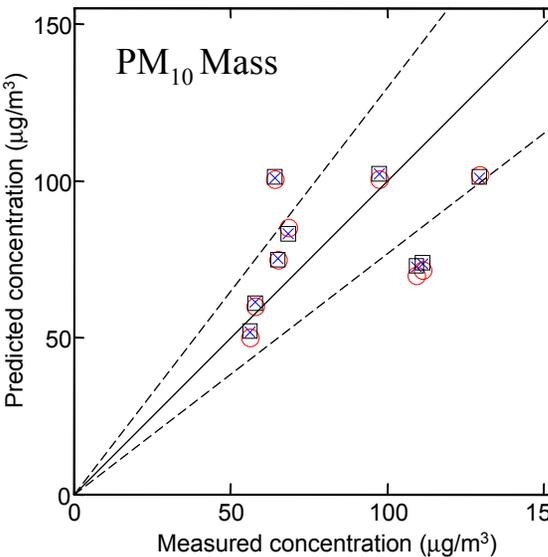
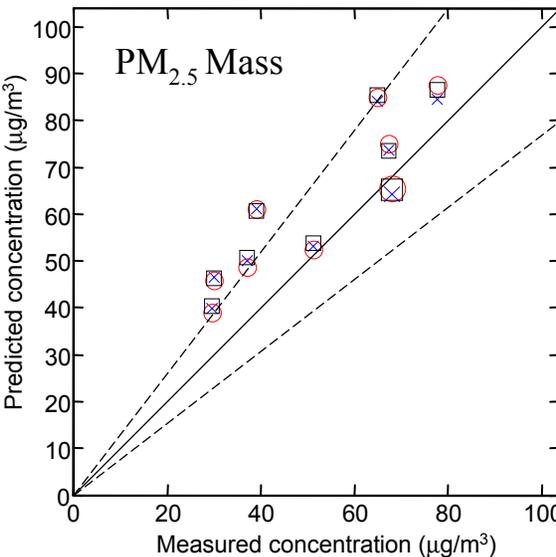
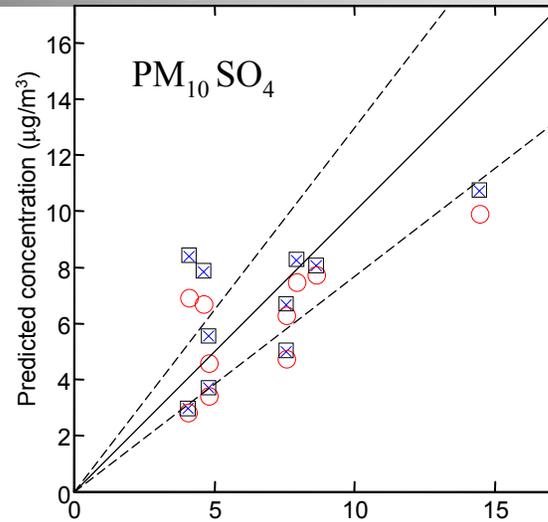
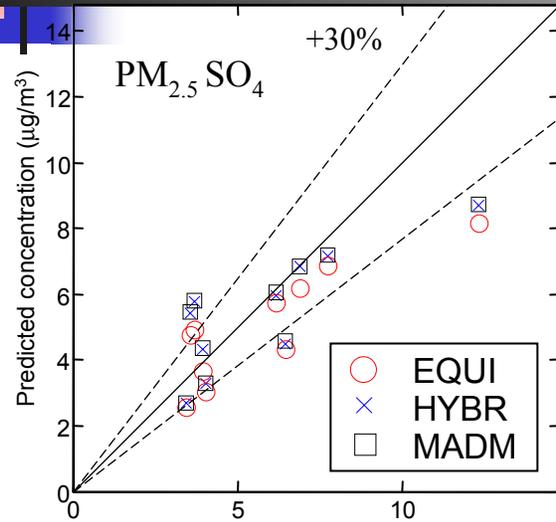
PM_{2.5} Ammonium Simulation (July 2001)



Click on map to start simulation.

Predicted vs. Measured PM

(Sulfate and Total PM)

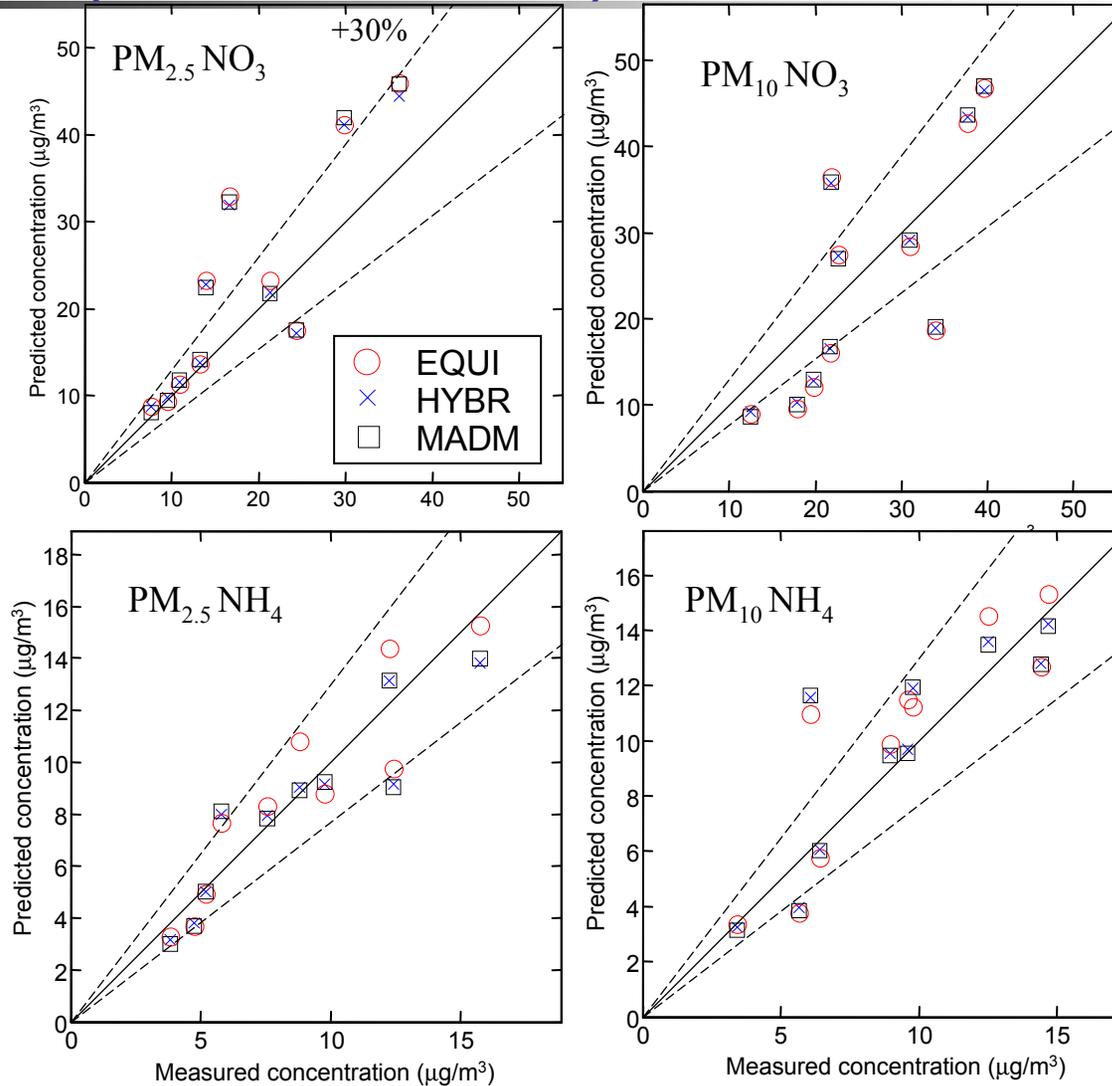


EQUI - Bulk Equilibrium Model
 Capaldo et al. (2000)
Atmos. Environ. 34:3617

HYBR - Hybrid Model
 Capaldo et al. (2000)
Atmos. Environ. 34:3617

MADM - Dynamic Model
 Pilinis et al. (2000)
Aerosol. Sci. Technol. 32:482

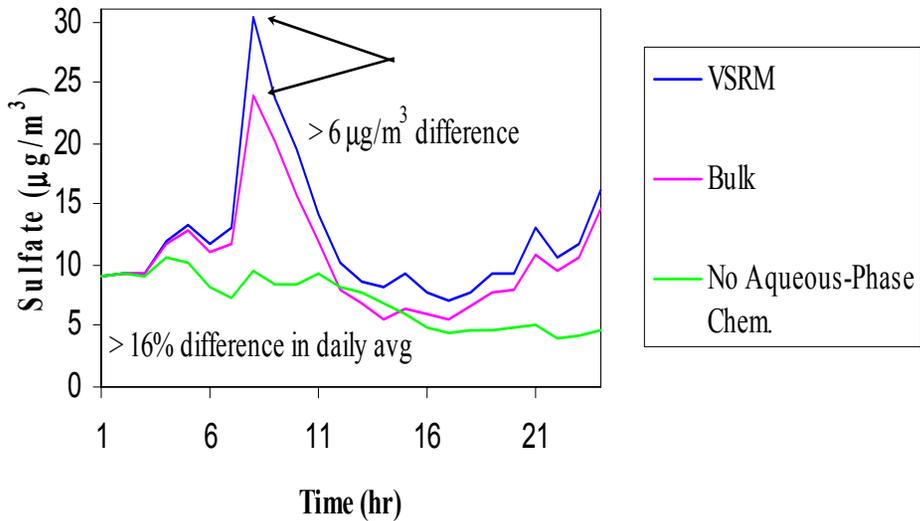
Predicted vs. Measured PM (Nitrate and Ammonium)



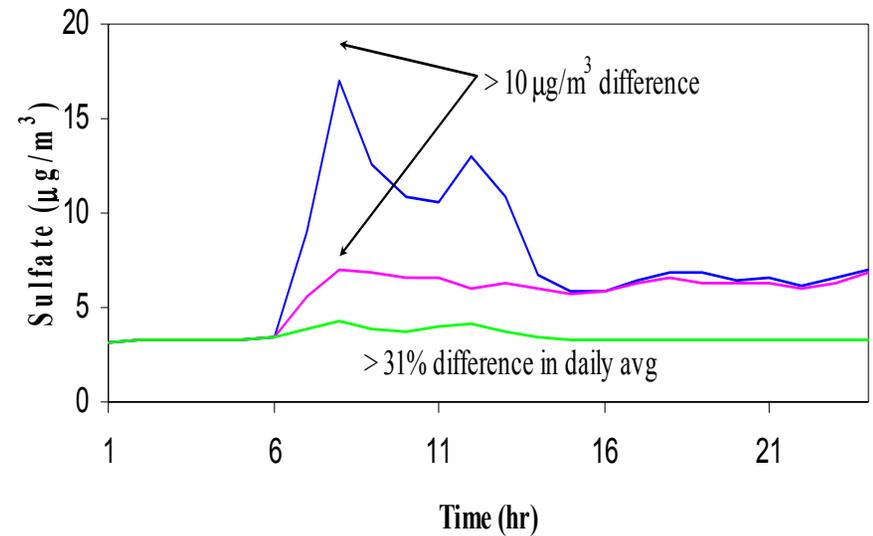
Aqueous Module

Effects of Higher Size-Resolution

PM10 Sulfate - Long Beach - Oct. 18, 1995



PM10 Sulfate - (18,15) - Oct. 18, 1995



Use of Trajectory-Grid Approach for the Condensation Equation

Condensation equation:

$$\frac{\partial q_i}{\partial t} = H_i q - \frac{1}{3} \frac{\partial H q_i}{\partial \mu}$$

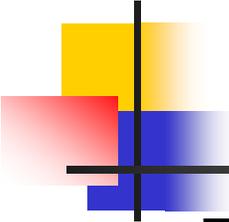
H_i is condensation rate of species i , $H = \sum H_i$, $q_i \Delta \mu$ is concentration of i in section of size $\Delta \mu$, and μ is the logarithm of the diameter

Analytical solution along trajectory $\mu^{n+1} = \mu^n + H \Delta t / 3$ with constant H_i :

$$q_i(\mu, t + \Delta t) = q_i(\mu, t) + \frac{H_i}{H} q(\mu, t) (e^{H \Delta t} - 1) \quad \text{for } H \neq 0$$

$$q_i(\mu, t + \Delta t) = q_i(\mu, t) + H_i q(\mu, t) \Delta t \quad \text{for } H = 0$$

Time step selection scheme: $q(H_{n+1} - H_n) \Delta t \leq \varepsilon$



Limitation on Hydrogen Ion Flux

- The hydrogen ion flux can be calculated from the fluxes of the inorganic gases

$$J_{H^+,k} = 2J_{H_2SO_4,k} + J_{HNO_3,k} + J_{HCl,k} - J_{NH_3,k}$$

- To avoid unrealistically large evaporation rates and reduce stiffness, the hydrogen flux is kept within a critical value by modifying the flux of the acids or bases

$$J_{i,k}^* = \frac{J_{i,k}}{Q_k} \begin{cases} i=HNO_3, HCl & \text{if } J_{H^+,k} > \gamma \\ i=NH_3 & \text{if } J_{H^+,k} < -\gamma \end{cases}$$

where γ is 10% of the hydrogen ion concentration per second

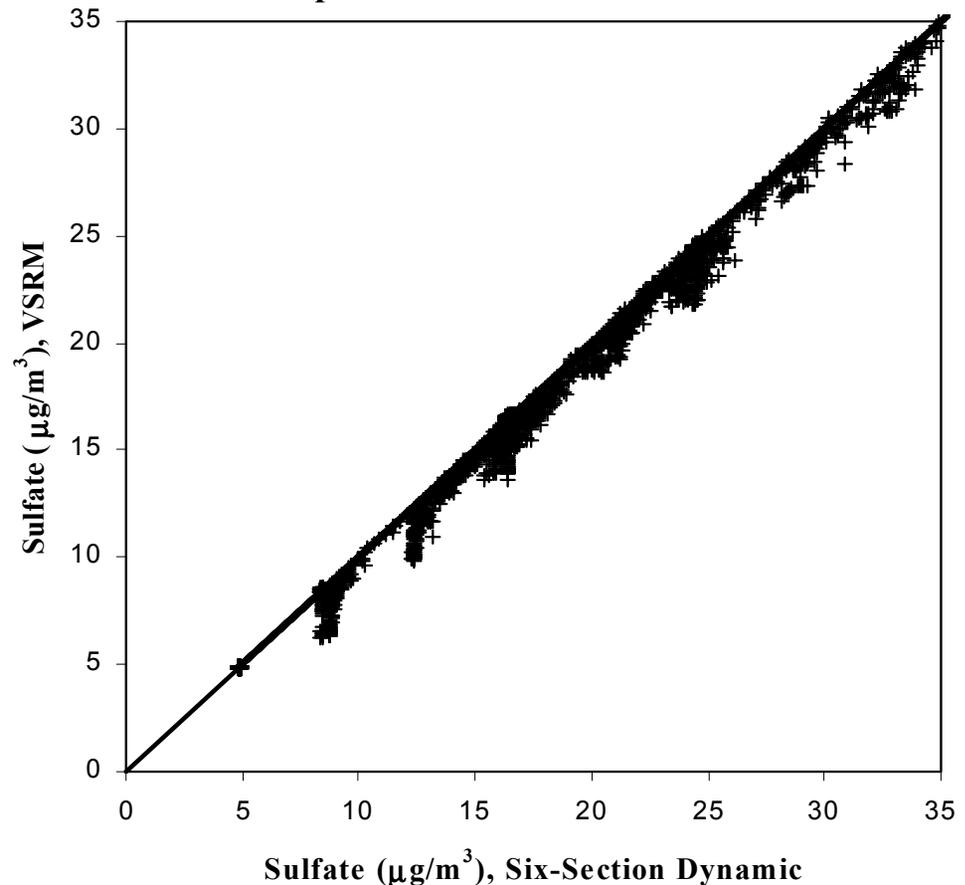
VSRM Aqueous-Phase Chemistry

Module*

- Simulates mass transfer between the phases and aqueous chemistry
- Treats 50 aqueous-phase and 21 gas-phase species and includes 109 aqueous phase reactions
- Choice of droplet resolution: bulk, 2-section size resolution, and variable size resolution based on simulated conditions
- Faster than six-section dynamic approach by a factor of 15

*Fahey, K. and Pandis, S. 2001. Optimizing model performance: variable size resolution in cloud chemistry modeling. *Atmospheric Environment* 35, 4471-4478.

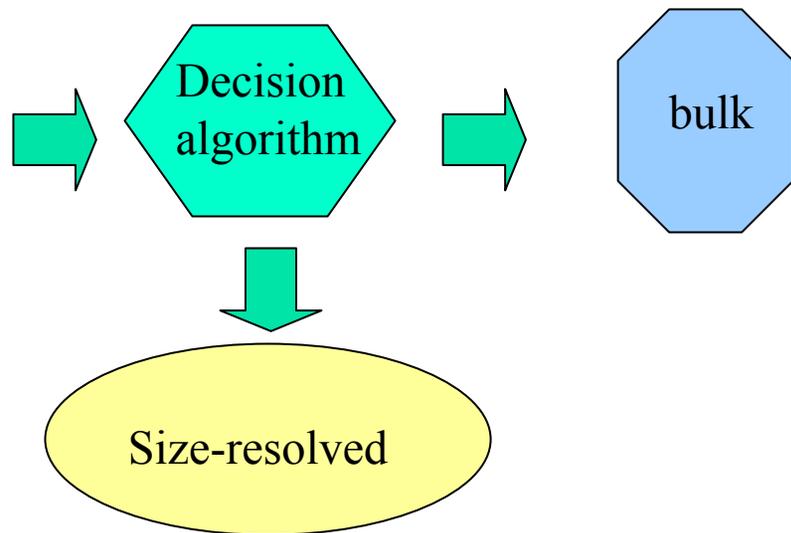
Comparison of Model Predictions^a



^aSulfate predicted by the VSRM vs. sulfate predicted by a six-section size resolved model. The 1:1 line is shown. Average VSRM sulfate predictions are within 3% of the more highly resolved model.

Aqueous-Phase Chemistry Variable Size Resolution Model (VSRM)

Inputs: Liquid water content, alkalinity of crustal aerosol, gas-phase concentrations of SO_2 , H_2O_2 , HNO_3 , and NH_3



Model	Average CPU Time per simulated hour (sec)	Standard Deviation (sec)	Model to VSRM ratio
Six-Section, Dynamic Transfer of HNO_3	20	33	15
VSRM, Immediate Dissolution of HNO_3	1.3	1.5	1
Bulk, Immediate Dissolution of HNO_3	0.9	1.3	0.7

Improving the Weighting Scheme for the Equilibrium Method

The fraction, $f_{i,k}$, of total flux of species, i , between gas and aerosol phases that condenses onto or evaporates from an aerosol size section, k :

$$f_{i,k} = \frac{2\pi N_k d_k D_i (c_i - c_i^{eq}) / (\beta_k + 1)}{\sum_k 2\pi N_k d_k D_i (c_i - c_i^{eq}) / (\beta_k + 1)}$$

N_k : number of particles in the section k

d_k : mean diameter of particles in the section k

D_i : diffusivity of species i

c_i : bulk gas-phase concentration of species i

c_i^{eq} : equilibrium concentration of species i at the particle surface

$$\beta_k = 2\lambda a d_k$$

λ : mean free path of air

a : accommodation coefficient

Assuming that c_i^{eq} is independent of particle size

$$f_{i,k} = \frac{N_k d_k / (\beta_k + 1)}{\sum_k N_k d_k / (\beta_k + 1)} = f_k$$

Composition-dependent c_i^{eq} with the pseudo-ideal solution assumption

$$f_{i,k} = \frac{N_k d_k (c_i - x_{i,k} c_i^*) / (\beta_k + 1)}{\sum_k N_k d_k (c_i - x_{i,k} c_i^*) / (\beta_k + 1)}$$

$x_{i,k} \leftarrow x_{i,k}$ from the previous time step